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## TESTS OF A MECHANISM FOR $H_2S$ RELEASE DURING COAL PYROLYSIS

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# Tests of a Mechanism for H<sub>2</sub>S Release during Coal Pyrolysis

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## Abstract

We have used a temperature programmed, gas evolution technique to compare H<sub>2</sub>S from coal and from pyrite in the presence of minerals or polymers. Pyrite decomposition in coal with H<sub>2</sub>S release can be observed directly only if carbonate minerals, particularly iron-containing carbonates, are absent. Two distinct chemical mechanisms are required to model conversion of pyrite in coal to H<sub>2</sub>S and pyrrhotite. Initially a reaction at pyrite grain surfaces (shrinking core model) occurs that is controlled by the rate of iron movement toward crystallite centers and by hydrogen-donor availability. Tar evolution (as indicated by methane-plus-ethane) also requires H-donors. Organic free radicals compete so efficiently for this scarce commodity that the rate of pyrite decomposition slows. At a 10 K/min heating rate, the rate of H<sub>2</sub>S release by the H-donor mechanism reaches a maximum at 700 K and then decreases. Unimolecular decomposition of coal pyrite to FeS and S<sub>2</sub> then occurs sharply at 830 K. Coal pyrolysis products effectively capture S<sub>2</sub>, and the rate of H<sub>2</sub>S release matches that of sulfur release from pure pyrite in a vacuum (0.07 mg-S/cm<sup>2</sup>/min at 773 K). The high temperature H<sub>2</sub>S evolution peak from coal is often distorted by inorganic sulfide hydrolysis and reversible H<sub>2</sub>S capture, both of which depend on a rapidly changing [H<sub>2</sub>S]:[H<sub>2</sub>O] ratio. Water release from clays affects H<sub>2</sub>S evolution. By monitoring CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>-plus-C<sub>2</sub>H<sub>6</sub> as well as H<sub>2</sub>S, we can provide a consistent picture for a particularly difficult case, the Illinois #6 coal from the set of Argonne coals. Modified Ill #6 coal (acid-leached or pyrite-free), spiked samples, and polymers were pyrolyzed with inert or reactive gas sweeps to provide supporting data.

## Introduction

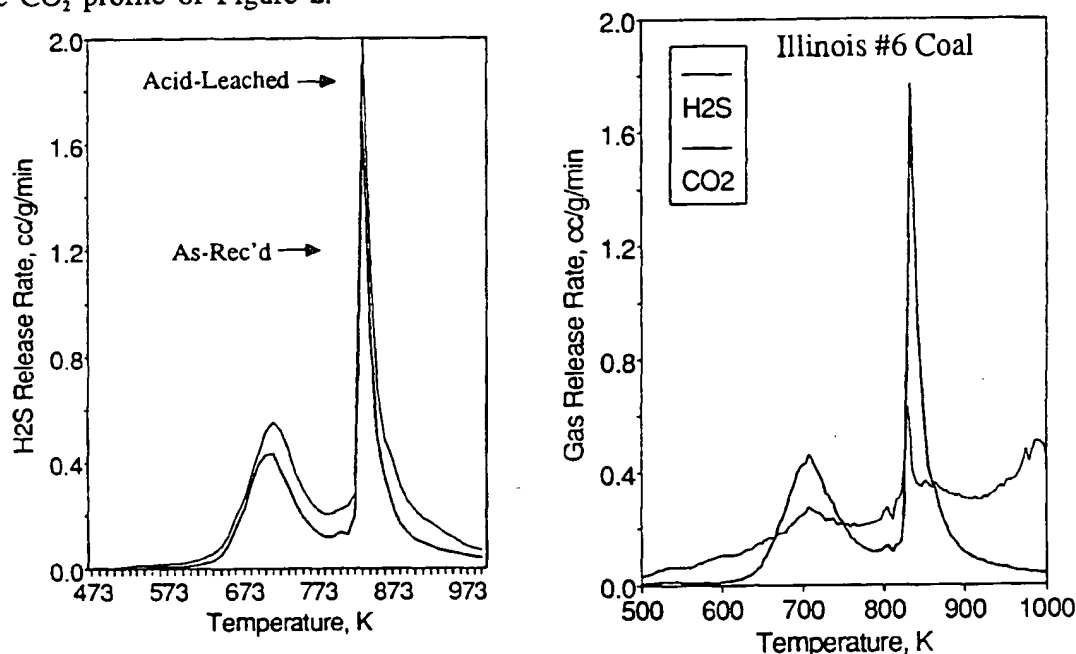
The release of sulfur-containing compounds from coals during pyrolysis has been of continuing interest in our laboratory and others. The volume of literature on this subject is great and occasionally contradictory. The choice of authorities can bias introductory comments. Oh et al.<sup>1</sup> have summarized literature preferences from our laboratory. In general, our biases match those of Khan.<sup>2</sup>

Hydrogen sulfide is the principal sulfur species released during coal pyrolysis. Illinois #6 coal from the set of Argonne coals, probably the best characterized high sulfur coal available,<sup>3</sup> was chosen to test our understanding of coal sulfur chemistry. We used a procedure for temperature programmed gas evolution (at 10 K/min) somewhat similar to the TGA/MS and TGA/FTIR used by others.<sup>4,5</sup> We used a small all-quartz pyrolysis tube, a large sample size (0.5 g), and argon sweep at 20 cc/min. A quadrupole MS detected H<sub>2</sub>S and other gases; no weight changes were recorded.<sup>1</sup> Conditions were varied, and conclusions that follow are based on the gas evolution data.

## Results and Discussion

Figure 1 shows release of H<sub>2</sub>S from as-received and from acid-leached Illinois #6 coal. Capture of H<sub>2</sub>S by carbonate minerals often interferes with its detection; this

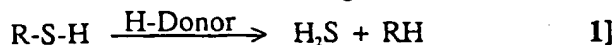
reaction has rarely been adequately appreciated. Only a weak acid treatment is needed to remove mineral carbonates (we used 5% acetic acid) but enough time to wet the particle completely must be allowed (18 hr at 373 K). Figure 2 shows that CO<sub>2</sub> release during coal pyrolysis matches H<sub>2</sub>S release, as one would expect if carbonate minerals react with H<sub>2</sub>S. Thermodynamics for H<sub>2</sub>S capture by calcite or dolomite is borderline at best, and our spiking experiments proved these minerals ineffective, as shown previously.<sup>26</sup> Apparently the iron component captures H<sub>2</sub>S. Ankerite (ferroan dolomite), siderite, and synthetic FeCO<sub>3</sub> were all reactive, but only ankerite had sufficient thermal stability to give the CO<sub>2</sub> profile of Figure 2.



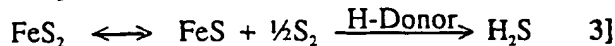
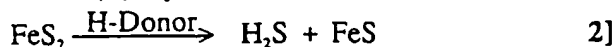
Figures 1 and 2. Gas evolution profiles showing the impact of carbonate minerals on Illinois #6 coal pyrolysis at 10 K/min heating rate.

Table 1. Reactions controlling H<sub>2</sub>S evolution.

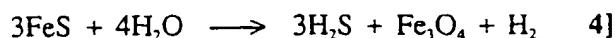
I. Formation from (A) Organics:



(B) Pyrite:



(C) Hydrolysis:



II. Capture by (A) Minerals (M = Fe):



(B) Organic Intermediates:

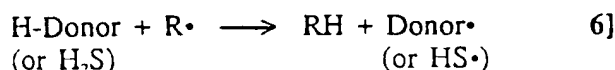


Table 1 lists the set of reactions that apply to H<sub>2</sub>S evolution from Illinois #6 coal. To simplify the complicated chemistry, we can use acid-leached coal and eliminate reaction 5]. Those experiments using coal free of carbonates proved most informative. We define pyrite as FeS<sub>2</sub>, recognizing that FeS<sub>2</sub> in coal has several forms and the name is imprecise. Highly crystalline FeS<sub>2</sub> and a specially prepared fram-boidal material<sup>7</sup> behaved similarly as additives in the work described, if air oxidation was carefully avoided.

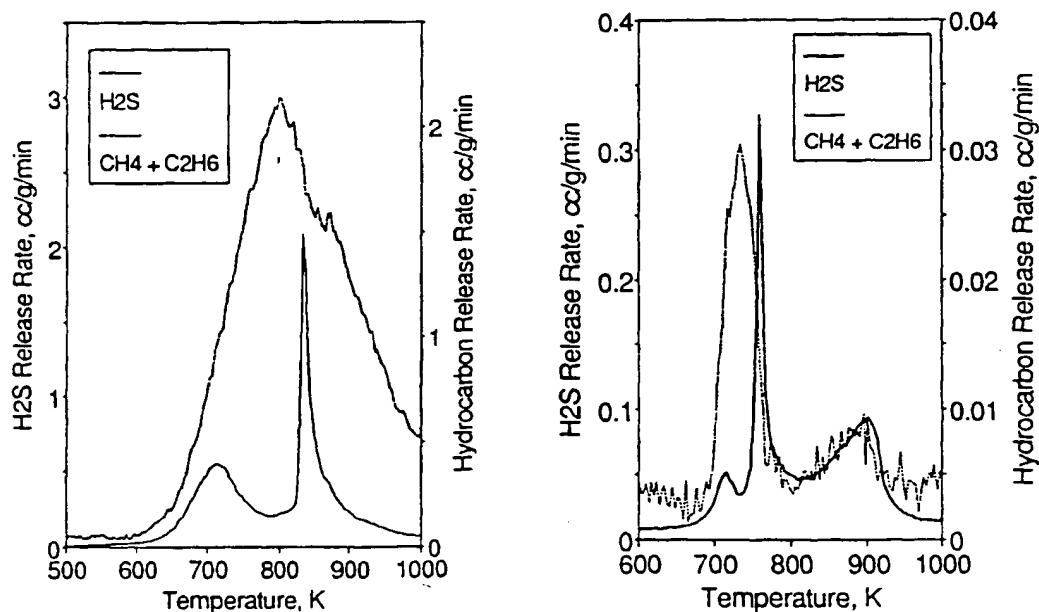
A first thought on viewing Figure 1 is that low temperature H<sub>2</sub>S release from coal is due to

decomposition of organic sulfur compounds (reaction 1]) and that high temperature release is due to pyrite decomposition (reactions 2] or 3]). However, it is well established that pyrite contributes to both low and high temperature release.<sup>1,2</sup> Khan<sup>2</sup> writes the following expression for [H<sub>2</sub>S] on heating various coals to 773 K under his experimental conditions:

$$[\text{H}_2\text{S}] = 0.17(\text{Coal}_{\text{pyr-S}}) + 0.40(\text{Coal}_{\text{org-S}}) ; \quad R^2 = 0.94 \quad 7]$$

By default, reaction 2] seems to best characterize low temperature formation of H<sub>2</sub>S from pyrite. It is a surface reaction that depends on the availability of *in-situ* generated H-donors. A shrinking core model with the rate of iron migration toward crystallite interiors controlling the quantity of active sulfur at the interface<sup>8,9</sup> fits the data. Both reaction 1] and 2] require H-donors formed from the coal, so inorganic and organic sources of H<sub>2</sub>S are coupled. Furthermore, hydrocarbon formation competes for donors (reaction 6]). Methane-plus-ethane, the principal hydrocarbons released from coal, can be used to follow this competing reaction. Since methane release signifies re-solidification of a plastic coal,<sup>10</sup> H-donor mobility also may diminish in this temperature range. H<sub>2</sub>S added to the sweep gas was not captured, indicating condensed phase chemistry.

As acid-leached coal heats up, H-donors form, generating H<sub>2</sub>S until organic free radical precursors of gas and tar become so abundant that they consume most of the mobile H-donor capacity (Figure 3). H<sub>2</sub>S release then drops off. At about 830 K, a new pyrite decomposition reaction dominates, unimolecular decomposition, reaction 3]. Active sulfur forms and reacts aggressively with hydrogen-donors or hydrocarbon precursors (note an inflection at 830 K in the CH<sub>4</sub>-plus-C<sub>2</sub>H<sub>6</sub> curve of Figure 3). The sharp decomposition occurs just at the temperature where pyrite decomposes in a vacuum (with a rate equal to 0.07 mg-S/cm<sup>2</sup>/min at 773 K).<sup>8</sup> Coal pyrolysis products remove sulfur effectively, and the reverse reaction is eliminated. High temperature H<sub>2</sub>S release thus occurs at a lower temperature than from pure pyrite in a TGA apparatus under 1 atmosphere of inert gas.



Figures 3 and 4. Evidence for the competition with organic free radicals for H-donors: (3) Acid-leached Ill #6 and (4) polystyrene/pyrite/firebrick pyrolysis.

It should be possible to see the two pyrite decomposition modes in simpler systems. An inert mineral phase (firebrick), a pure organic phase with no organic sulfur (polystyrene), and analytically pure pyrite with no air contact would be the ideal case. Figure 4 shows that under our standard pyrolysis conditions this ideal system does result in two H<sub>2</sub>S releases with a minimum at the CH<sub>4</sub>-plus-C<sub>2</sub>H<sub>6</sub> maximum-release temperature. A distinct H<sub>2</sub>S loss as pyrrhotite becomes increasingly stoichiometric also is seen in Figure 4. This reaction merges into the broad organic H<sub>2</sub>S release when coal pyrolyzes. Results of Figures 3 and 4 are generally consistent, although hydrocarbons and hydrogen-donors form over a narrower temperature range in our "ideal" system.

The high temperature H<sub>2</sub>S release peak is so narrow that dispersion and detector sampling frequency affect its appearance. Charring and reaction 4] distort the peak. The surface layer of inorganic sulfides form by capture of H<sub>2</sub>S seems particularly susceptible to hydrolysis. Sweep with dry argon, water-saturated argon, and steam give significantly different high temperature H<sub>2</sub>S releases. Both the absolute quantity of water (degree of dilution) and the [H<sub>2</sub>S]:[H<sub>2</sub>O] ratio matter. Water sources include reaction 5], the water gas shift reaction, and illite dehydration.

The variety of reactions in Table 1 offer opportunities to adjust H<sub>2</sub>S evolution during coal pyrolysis within a limited range. Water, reactive solids, and organic intermediates all interact with H<sub>2</sub>S or H<sub>2</sub>S precursors to an extent that depends on reaction conditions, coal type, and the details of the pyrolysis process.

#### Acknowledgement

Valuable comments and observations of R.W. Taylor, A.K. Burnham, R.W. Crawford, and A.E. Lewis are gratefully acknowledged. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-Eng-48.

#### References

1. Oh, M.S., Burnham, A.K. and Crawford, R.W. Preprints, Div. Fuel Chem., Am. Chem. Soc. 1988, 33(1), 274
2. Khan, M.R. Fuel 1989, 68, 1439
3. Vorres, K.S. Energy & Fuels 1990, 4, 420
4. Jüntgen, H. Fuel 1984, 63, 731
5. Serio, M.A., Solomon, P.R. and Carangelo, R. Preprints, Div. Fuel Chem., Am. Chem. Soc. 1988, 33(2), 295
6. Wong, C.M., Crawford, R.W. and Burnham, A.K. *ibid.* 1984, 29(3), 317
7. Berner, R.A. Econ. Geology 1969, 64, 383
8. Lambert, J.M. "Transformation of Pyrite to Pyrrhotite and Its Implications in Coal Conversion Processes" PhD Thesis, The Pennsylvania State University, 1982; 175pp
9. Condit, R.H., Hobbins, R.R. and Birchenall, C.E. Oxidation of Metals 1974, 8, 409
10. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V. Energy & Fuels 1988, 2, 405